



FIG. 2. Comparison of temperature effects on peroxide development in gamma irradiated methyl oleate.

Although gamma-irradiation effectively influences oxidation at low temperature, thermal effects are evident as temperatures are raised. This was shown by a series of oxidations made over temperature ranges from 7.5°C. to 55°C. The rate and extent of peroxide development at two temperatures are shown in Figure 2. This shows that the thermal effect is quite marked and implies that substantial peroxide values can be achieved in relatively shorter periods of time when both gamma radiation and thermal effects are operative. In Table IV are values for the oxidation products from 100-hr. oxidations at varying temperatures under the influence of gamma radiation. A plot of peroxide values *versus* temperature would

TABLE IV

Temperature Effect on Oxidation of Methyl Oleate Irradiated with 118 r/sec. Gamma Radiation for 100 Hours

Temperature, °C.	Peroxide value me/kg	Carbonyl value mmol/kg	$E_{1\text{cm}}^{1\%}$ 224 m μ
7.5.....	720	200	22
29.....	1450	475	27
36.....	1720	440	24
42.....	2160	—	36
56.....	2450	618	39.5

show that the relation is essentially linear throughout the temperature range studied. The maximum peroxide value has not been exceeded for any of the time-temperature conditions noted.

Table IV shows that total carbonyl values continued to increase with increased temperature. Since the peroxides were not reduced before the carbonyl value determinations were made, it is not possible to say that the measured total carbonyl value was entirely due to those initially present or whether some carbonyls were formed by peroxide decomposition by the agents and conditions used in the determination. It is to be noted however that the $E_{1\text{cm}}^{1\%}$ values at 224 m μ did not increase in the same proportion. There is good reproducibility and agreement between the total carbonyl values and peroxide values in samples treated in a comparable manner. Two samples irradiated for 67 and 68.5 hrs. at 65°C. have peroxide values of 2340 and 2345, respectively, and total carbonyl values of 640 and 622, respectively. The $E_{1\text{cm}}^{1\%}$ values at 224 m μ vary somewhat although they do not represent a great difference in concentration of the materials causing this absorption.

These studies have shown that gamma radiation influences the oxidation of unsaturated materials such as oleic acid and methyl oleate. It is of interest to learn whether the oxidation products resemble or differ from those provided by thermal oxidation with regard to kind and position. Studies are in progress to establish this information.

Summary

1. Gamma radiation from Cobalt 60 influences the oxidation of oleic acid and methyl oleate even at low temperatures.
2. Determination of peroxide values, carbonyl values, and the $E_{1\text{cm}}^{1\%}$ values at 224 m μ revealed that high peroxide values could be obtained but that secondary products are formed in appreciable quantities.
3. The products causing absorption at 224 m μ may be α,β -unsaturated ketones. The level of these substances can be increased by irradiation-oxidation in the presence of metal soaps such as cobalt stearate.
4. Irradiation-oxidation of methyl oleate through a series of temperature ranges from 7.5°C. to 55°C. reveals a marked thermal activation effect. Peroxide values of 2000 me/kg or greater are obtained in 100 hrs. of reaction time.

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CORRECTION

B. Sreenivasan, now at Ohio State University, Columbus, writes as of March 3, 1956, that an error appears on page 63, in Table V, of the February 1956 issue, for the article entitled "Studies on Castor Oil. I. Fatty Acid Composition of Castor Oil," by himself, N. R. Kamath, and J. G. Kane, University of Bombay, India. Below bromometric the wording should be 31–33°C., 60 min. (not 60 mm. as published).